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SOLID PROPELLANT COMBUSTION MECHANISM RESEARCH

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13. ABSTRACT

This annual report highlights the progress being made on several concurrent solid propellant combustion mechanism researches. Studies of nitrocellulose-base propellants have produced a broad range of experimental results for platonized and unplatonized propellants. The corresponding mathematical models consider the flame zone processes controlling temperature sensitivity, extinguishment limits, and burning rate. The analytical studies of ignition and burning of porous propellants are producing good agreement with data, new insights into the combustion processes, and establishing regimes where steady-state burning rates are achievable. The work of nonsteady burning has progressed to the point that rocket motor transients can be predicted and dynamic burning rates in a variable throat area, low L* motor can be measured; this work has progressed from the research phase to the development stage. Sub-micron pyrophoric aluminum is being investigated as a means of increasing propellant burning rate.

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1.0 TECHNICAL OBJECTIVES

The goal of this research on solid propellant combustion is to acquire a fundamental understanding of the burning processes. The attainment of this goal is leading to the development of theories that first, take account of all the important physical and chemical processes in the flame, and, second, are capable of predicting burning rates and rocket motor performance quantitatively over the entire range of parameters of interest.

This research is revealing the important characteristics of the flame zones of solid propellants and provides information on combustion processes that underlies all practical combustion problems. This includes not only the prediction and control of steady-state burning rates, but also the prediction of nonsteady burning rates, engine instabilities, propellant ignitability, thrust transients, thrust termination by flame extinction, and conditions to achieve ultra-high burning rates.

The basis for our approach is that four kinds of research are necessary if useful results are to be obtained: (1) Diagnostic experiments -- surface temperature, flame spectra, etc. -- are required to provide the basis for realistic physical models; (2) Physical-chemical measurements of various properties and processes -- pyrolysis rates, reaction kinetic data, etc. -- are required to obtain quantitative deductions from the theoretical analysis; (3) Theoretical analyses of burning rates based on realistic, not artificial, physical models must be advanced and solved in order to lead to useful correlations or predictions; (4) Performance measurements -- burning rates of propellants under various conditions, extinction characteristics, etc. -- are required in order to test the validity of the theories that are evolved. The program involves all four of these elements, and consequently it involves theoretical work, physical-chemical laboratory work, and combustion tests of various kinds.

The recent achievements of the current program have been reported in the publications listed in Section 3.0. The achievements on each of the continuing objectives can be summarized as follows. The studies of nitrocellulose-base propellants (Continued Objective 1) have produced a broad range of experimental results (i.e., publications 1, 2, and 3 in Section 3.1; publication 4 in Section 3.2; and publications 1 and 2 in Section 3.3) for platonized and unplatonized propellants and mathematical models that consider the flame zone processes controlling temperature sensitivity, extinguishment limits, and burning rate. The analytical studies (see publications 3 and 5 in Section 3.2) of ignition and burning of porous pro-

pellants (Continued Objective 2) are producing good agreement with data, new insights into the combustion processes, and establishing regimes where steady-state burning rates are achievable. The work on nonsteady burning (Old Continued Objective 3) has progressed to the point that we can predict rocket motor transients and can obtain measured dynamic burning rates in our variable throat area, low L* motor. Since this work has progressed from the research phase (see publications 1 and 2 in Section 3.2) to the development stage*, we are considering that the requirements of Old Objective 3 have been satisfied, and thus we are dropping it in 1974. The work on various combustion mechanisms (New Objective 3) has been centered primarily on investigating the effect of sub-micron pyrophoric aluminum as a means of increasing propellant burning rate.

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*The following publications are examples of how one of the propulsion companies, the Huntsville Division of the Thiokol Chemical Corporation, is applying this research:
Stokes, B. B., "Effects of Dynamic Burning on Operation of a Throttleable Fuel Generator for Fuel Rich Propellants," <u>Proceedings of 8th JANNAF Combustion Meeting</u>, CPIA publication 220, Vol. I, Nov. 1971, pp. 505-525.
Stokes, B. B. and Aycock, W. C., "Analysis of Transient Ballistic Test Data in the Development of High Rate High Exponent Composite Propellants," <u>Proceedings of 9th JANNAF Combustion Meeting</u>, CPIA Publication 231, Vol. I, Dec., 1972, pp. 49-65.

2.0 SUMMARY OF SELECTED RECENT RESULTS

2.1 Plateau and Super-Rate Burning of Double Base Propellants

This study is directed at understanding how organic lead salts used as catalysts alter the burning mechanisms of double base propellants (i.e., two nitrate esters inter-diffused) to produce burning rate increases (known as super-rate burning) and domains of reduced burning rate pressure sensitivity (known as plateau burning). Simultaneously, these same lead salts greatly reduce the temperature sensitivity of burning rate in the super-rate range. These effects are of great practical interest since they provide design flexibility and yield performance which is largely constant over a prescribed range of operating pressures and initial temperatures.

The experimental investigations were carried out with particulate nitrocellulose (PNC) and trimethylolethane tri-nitrate (TMETN) double base propellants instead of with the more hazardous-to-formulate nitrocellulose (NC) and nitro-glycerin (NG) propellants which are more widely used. Experiments confirmed that the burning characteristics of NC/NG and PNC/TMETN propellants are very similar. Thirty-two propellants with systematic variations in additives (including metallic lead powder, lead oxide, lead salicylate, metallic copper powder, copper salicylate, finely divided carbon, ammonium polyphosphate, oxamide, and ammonium per-chlorate), particle size, and degree of dispersion were specially formulated for this study. The lead salts produced burning rate increases up to 300%.

The combustion wave is seen to consist of four identifiable zones: (1) the surface reaction layer; (2) the fizz zone, characterized by the first steep temperature gradient in the gas phase; (3) the dark zone, in which the temperature is almost constant; and, finally, (4) the luminous flame zone, which includes the final combustion processes. This study reveals that the burning-rate of double base propellants is governed by the chemical reactions that occur in a very thin surface reaction layer ($\sim 100\mu$ at 1 atm, $\sim 20\mu$ at 20 atm) and fizz zone ($\sim 200\mu$ at 1 atm, 100μ at 20 atm).

Diagnostic experiments were carried out to determine the burning rate behavior of the specially formulated propellants over a pressure-range from 0.1 atm to 100 atm. The gas phase structure, burning-surface structure, temperature profiles in the reaction zones, and global effects were examined using high speed photography, micro-thermocouples (bead size 4μ), burning rate measurements, and burning extinction by rapid depressurization.

The micro-thermocouple experiments revealed that the addition of lead salts has only very small effects on the

surface temperature (T_s) and the heat release at the surface (Q_s). For example, at 20 atm, the addition of a mixture of 1% lead salts and 1% copper salts increases T_s from 345°C to 375°C, representing less than 10% increase in (T_s - T_0), and produces no detectable change in Q_s (90 cal/g). However, these same additives significantly increase the temperature gradients in the fizz zone, e.g., between 10 and 20 atm, increases of 70% to 100% over the noncatalyzed propellant were measured.

The dark zone reaction mechanisms were studied by means of high speed photography. During super-rate burning of a catalyzed propellant, the luminous flame is displaced further from the burning surface than the luminous flame of noncatalyzed propellants. For example, at 20 atm, the luminous flame is positioned 0.25 cm above the burning surface for a noncatalyzed propellant, and 1.1 cm for a catalyzed propellant. From such observations it was concluded that the heat feedback from reactions beyond the fizz zone to the burning surface does not affect significantly the burning rate.

Burning surface observations using high speed photography and extinguished propellant samples revealed that, when lead salts are added to the propellants, large amounts of solid carbon are formed on the surface at low pressures where super-rate burning occurs. The quantity of carbon decreases with increased pressure, and the super-rate burning diminishes at the same time.

As a result of this study, we summarize the important changes attributed to the lead salts as follows. Lead salts directly affect the surface reaction layer (∿ 20μ thick at 20 atm), where the lead salts decompose ultimately into finely-divided metallic lead or lead oxide particles. The decomposition products of the lead salts react with the nitrate esters in the surface reaction layer, altering their decomposition mechanism so as to produce an increased amount of solid carbon on the surface. Although these reactions are not known in detail, the shift in mechanism surprisingly does not significantly alter the net exothermicity. The presence of lead salts accelerates the fizz zone reactions and thereby increases the heat feedback to the surface; this produces super-rate burning.

We conclude that these actions of the lead salts to produce increased carbon at the propellant surface and the acceleration of the fizz zone reactions are directly coupled as follows. The portion of decomposed organic molecules which appears at the surface in the form of carbon rather than readily oxidizable aldehydes could reduce the effective fuel: oxidizer (aldehyde: NO_2) ratio. This increased NO_2 proportion constitutes a shift in equivalence ratio toward

the stoichiometric value. Such a shift for NO_2/aldehyde mixtures results in a greatly accelerated reaction rate. This is the proposed mechanism of fizz zone reaction rate acceleration.

The degree of super rate decreases as the burning rate increases (producing the plateau effect), since the time available for the initial catalytic action in the surface reaction layer decreases. This decrease in available time is a consequence of the higher burning rate and the decreased thermal wave thickness. Thus, since the fraction of the reactants affected by the lead compounds (and excess concentration of NO_2) decreases, the reaction rate in the fizz zone approaches the normal reaction pathway, and then super-rate burning diminishes.

The burning rate model resulting from this study differs from the two previously published models. Our experimental evidence does not support Camp's theory (1958) of photo-sensitized subsurface reactions. Powling, et al (1971) hypothesized that carbon, formed when lead compounds are added, catalyzes the NO reduction in the gas phase; evidence in this study supports the conclusion that lead compounds act instead to increase the proportion of NO_2 in the fizz zone.

While this research is producing a reasonable explanation of super-rate burning, no firm explanation has been found for the termination of super-rate effects at the pressure where plateaus are measured, nor is there any experimentally-supported explanation in the literature. This is still an unfinished task and a very important one which will be carried out under continuing Objective 2.

2.2 Steady-State Burning of Porous Propellants by Means of a Gas Penetrative Mechanism

The burning rates of conventional high-energy solid propellants are usually limited by the thermal energy feedback that can be absorbed at the regressing solid surface. The normal deflagration rate of solid propellants usually ranges from 1 to 10 cm/sec under a pressure of 100 atmospheres, whereas the detonation wave speed of solid explosives or propellants usually ranges between 4000 to 8000 m/sec, which is about 100,000 times higher than the speed of deflagration. A large part of the broad intermediate range of steady-state speeds between normal deflagration and detonation, which could be very useful for various practical applications, is actually forbidden by the Rankine-Hugoniot relations for conventional propellants. Nevertheless, the usual theories do not take into account the case of using unconventional propellants or unconventional means of energy feedback. Finding a mechanism for entering this forbidden range with a constant-velocity wave is the main objective of this part of our studies. The burning of porous propellants offers the possibility of doing this.

The high burning speeds of porous propellants are mainly due to the penetration of hot product gases into the unburned portion. The strong heat feedback from the burned products to the unburned medium accomplished in this way augments the speed of flame propagation well above the normal deflagration rate.

To fill the wide gap between steady-state deflagration and steady-state detonation, other modes of energy transfer might be adopted, at least in principle. This study, however, is focused on flame propagation by a convective mode of heat transfer that we will describe as gas-penetrative. Unlike most of the previous investigations of the subject, which centered on hazards caused by the fast burning of porous propellant grains[1,2], the current work emphasizes the practical use of a porous propellant as the main combustible substance in obtaining high gasification rates.

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[1] Andreev, K. K. and Khariton, Yu B., "Experimental Investigation of the Combustion of Explosives," State Publishing House of Defense Industry, 1940, pp. 39-60.

[2] Korotkov, A. I., Sulimov, A. A., Obmenin, A. V., Dubovitskii, V. F. and Kurkin, A. I., "Transition of Burning to Detonation in Porous Explosives," <u>Journal of Combustion, Explosion and Shock Waves</u>, Vol. 5, No. 3, 1969.

It is known from past experience and from our previously published results obtained under ONR sponsorship, that gas-penetrative burning of porous propellants or explosives under strong confinement is inherently self-accelerating. However, under suitable physical conditions, where the driving pressure is constant and where the internal porous propellant structure and chemical properties are all properly selected, the internal pressure distribution generated by propellant gasification can produce a constant rate of gas penetration through the unburned portion, and may eventually give a constant speed of combustion-wave propagation. Experimentally, some evidence of steady gas-penetrative burning in porous propellants has been observed by several investigators.[3,4]

According to Taylor[3], remarkably rapid rates of burning of PETN, RDX and HMX powders have been observed to occur above a transition pressure, the value of which varies with the explosive material, particle size, and loading density of the powder. The transition from slow burning to rapid burning occurs at a lower pressure level when large particle sizes are used. This is due to the fact that large particles form large hydraulic pores, and hence the permeability of the explosive-powder charge is high. The transition from normal conductive burning into gas-penetrative convective burning is thus achieved at low pressures. Taylor also showed that he was able to change the speed of flame propagation by changing the conditions at the unburned end of the charge. He observed relatively constant speeds of flame propagation along a major portion of the powder charge.

A regime of stationary convective burning having a rate substantially above the normal burning rate has also been observed by Andreev[5] and Chuiko[6]. For example, they found that combustion of low-density PETN at high pressures can proceed in a stationary manner at a rate several tens of times greater than the normal conductive burning rate.

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[3] Taylor, J. W., "The Burning of Secondary Explosive Powders by a Convective Mechanism," The Faraday Society, Vol. 58, 1962.

[4] Bobolev, V. K., Margolin, A. D. and Chuiko, S. V., "Stability of Normal Burning of Porous Systems at Constant Pressure," Journal of Combustion, Explosion and Shock Waves, Vol. 2, No. 4, 1966.

[5] Andreev, K. K., "Thermal Decomposition and Burning of Explosives," Moscow-Leningrad, Gosenergoizdat, 1957.

[6] Andreev, K. K. and Chuiko, S. V., Zh F Kh, Vol. 37, No. 6, 1963.

Whether these observed results truly indicate stationary gas-penetrative burning is a question yet to be verified by burning extremely long charges of propellant under constant external pressure. Although these observations of stationary propagation may not prove the existence of a true steady state, they nevertheless indicate that the temporal change in the combustion wave is not very significant during the period of observed constant-speed propagation. The theoretical study of the steady-state propagating wave is therefore an interesting problem.

This research work is not only directed toward the determination of the combustion-wave speed and wave thickness. It also includes a study of the structure of a stationary combustion wave propagated by convection of hot product gases into the pores of the unburned propellant. In the meantime, from the derivation and study of the equivalent Rankine-Hugoniot relations for porous propellant, we would be able to see from the R-H diagram why it is possible to enter the "forbidden" speed range of the usual R-H diagram.

As a result of our studies we have shown theoretically that high-speed steady-state combustion waves in porous propellants do exist. The theoretical model describes the steady-state combustion-wave structure in gas-penetrative burning of a porous solid propellant. The flame speed has been shown to be the eigenvalue of a two-point boundary value problem. It is also shown analytically that the solution of this problem is unique. The jump conditions and an equivalent Rankine-Hugoniot relation for a general porous-propellant combustion wave was derived. It is found that the origin of the equivalent Hugoniot curve is shifted to a much higher pressure level due to the contribution of the thrust per unit area in the solid phase. This shift of origin in the R-H diagram significantly enlarges the allowed region for real burning rates. This explains why it is possible to enter the "forbidden" speed range of the usual R-H diagram by using porous propellants.

We have shown mathematically that all the conventional R-H properties are preserved when the new origin, based upon the apparent pressure and apparent density, is used. For example, the Mach number of the product gas is unity at both upper and lower Chapman-Jouquet points. The entropy of the gas presents a maximum at the lower C-J point but reaches a minimum at the upper C-J point, etc.

3.0 RECENT PUBLICATIONS UNDER ONR FUNDING

3.1 Manuscript Submission Since Last Renewal Proposal

1. Kubota, N., Ohlemiller, T. J., Caveny, L. H., and Summerfield, M., "The Burning Rate Flexibility of Plastisol Double Base Propellants," accepted for presentation at the Tenth International Symposium on Space Technology and Science, Tokyo, Japan, September 3-8, 1973.

2. Kubota, N., Ohlemiller, T. J., Caveny, L. H., and Summerfield, M., "Combustion Characteristics of Catalyzed Double Base Propellants," submitted to AIAA 12th Aerospace Sciences Meeting, Washington, D. C., Jan 30-Feb 1, 1974.

3. Kubota, N., Ohlemiller, T. J., Caveny, L. H., and Summerfield, M., "A Model of Super-Rate Burning of Catalyzed Double Base Propellants," submitted to 15th International Combustion Symposium, Tokyo, Japan, Aug 25-31, 1974.

4. Kuo, K. K. and Summerfield, M., "Generalized Steady State Solution for the Combustion of Porous Propellants," submitted to the AIAA Aerospace Sciences Meeting, Washington, D. C., Jan 30-Feb 1, 1974.

5. Mal'tsev, V. M. and Summerfield, M., "Investigation of the Spectral Radiation Characteristics of the Flame Jet of Nitrate-Ester Propellants Containing Platonizing Catalysts," submitted to Combustion Flame.

3.2 Publications That Have Appeared Since Submission of Last Renewal Proposal

1. Turk, S. L., Battista, R. A., Kuo, K. K., Caveny, L. H., and Summerfield, M., "Dynamic Responses of Solid Rockets During Rapid Pressure Change," Journal of Spacecraft and Rotkets, Vol. 10, No. 2, Feb 1973, pp. 137-142.

2. Battista, R. A., Caveny, L. H., and Summerfield, M., "Non-Steady Combustion of Solid Propellants," AMS Report No. 1049, Oct 1972, Princeton University, Princeton, N. J. (AD 753835).

3. Kuo, K. K., Vichnevetsky, R., and Summerfield, M., "Theory of Flame Front Propagation in Porous Propellant Charges Under Confinement," AIAA Journal, Vol. 11, No. 4, April 1973, pp. 444-451.

4. Kubota, N., Ohlemiller, T. J., Caveny, L. H., and Summerfield, M., "The Mechanism of Super-Rate Burning of Catalyzed Double Base Propellants," AMS Report No. 1087, March 1973, Princeton University, Princeton, N. J.

5. Kuo, K. K. and Summerfield, M., "Theory of Steady-State Burning of Porous Propellants by Means of a Gas-Penetrative Mechanism," AIAA Paper No. 73-221, AIAA 11th Aerospace Sciences Meeting, Washington, D. C., Jan 10-12, 1973.

3.3 Recent Publications and Presentations Under ONR Funding Prior to Last Proposal

1. Kubota, N., Caveny, L. H., and Summerfield, M., "Temperature Sensitivity of Double-Base Propellants," Proceedings of 8th JANNAF Combustion Meeting, Vol. 1, CPIA Publication 200, Nov 1971, pp. 387-401.

2. Kubota, N., Caveny, L. H., and Summerfield, M., "Combustion Processes in Double-Base Propellants," presented at the 1971 fall meeting of the Eastern Section of The Combustion Institute.

3. Kuo, K. K., Vichnevetsky, R., and Summerfield, M., "Combustion of Propellant by the Convective Mechanism," AMS Report No. 1000, June 1971, Princeton University, Princeton, N. J.

4. Caveny, L. H., "Review of Workshop on Temperature Sensitivity of Solid Propellant Burning Rate," Proceedings of the 9th JANNAF Combustion Meeting, Vol. II, CPIA Publication 231, Dec 1972, pp. 197-216.